

EFFECT OF STEAM DESORPTION ON MOLECULAR SIEVE ADSORPTION OF n-PARAFFINS

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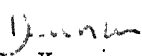
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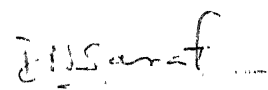
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CONTENTS

<u>CHAPTER</u>		<u>PAGE NO.</u>
	List of Figures	v
	List of Tables	vi
	Abstract	vii
1	Introduction	1
2	Lit erature Review	4
3	Experimental Investigation	9
4	Results and Discussion	15
5	Conclusions and Recommendations	31
	References	33
	Appendix	35

LIST OF FIGURES

<u>FIGURE NO.</u>		<u>PAGE No.</u>
1	Schematic Diagram of Experimental Set-Up	10
2	Breakthrough Curves at 200°C	16
3	Breakthrough Curves at 250°C	17
4	Variation of Adsorption Capacity with Cycle Number	18
5	Breakthrough Curves at 250°C Using n-Pentane as Desorbent	19
6	Breakthrough Curves at 250°C with Steam Rate 15 ± 1 gm/min.	20
7	Desorption Time in Different Cycles	21
A 1	Calibration Curve Between Refractive Index at 25°C and n-Paraffin wt. %	37
A 2	Agreement Between n-Paraffin Content and Refractive Index Measurements (2nd Cycle, 250°C)	38

LIST OF TABLES

<u>TABLE NO.</u>		<u>PAGE NO.</u>
1	n-Pentane Desorption Characteristics	24
2	Recovery of n-Paraffins in Different Cycles	25
3	Calculation of Height of Mass Transfer Zone	26

ABSTRACT

The feasibility of using steam as a desorbent for n-paraffins adsorbed on Linde Molecular Sieve-5A was investigated. The feedstock was kerosene obtained from Gujrat Refinery and experiments were conducted at two different temperatures for a fixed feed rate. Desorption with steam was carried out repeatedly for a number of cycles without intermediate reactivation. Substantial decrease in adsorption capacity of the sieves was observed. On reactivation, the sieves regained its original capacity. Performance of steam was compared with n-pentane as desorbent. More work is required before steam can be recommended as a possible desorbent. Height of mass transfer zone was also calculated.

CHAPTER 1

INTRODUCTION

The development of an effecient and economic process to separate long straight chain paraffins was necessitated by the requirement of a suitable feedstock to produce biodegradable detergents, now almost mandatory in many parts of the world. The use of n-paraffins as substrates for fermentation has a very high potential in the production of single cell protein¹ (referred as 'Petroproteins') for animal feeds. Besides this, n-paraffins are important raw materials for the synthesis of a variety of medicinal grade paraffins, plasticizers, fatty acids, secondary alcohols, olefins and aldehydes.

In the last few years, the demand for the n-paraffins in India has steadily increased at the rate of 15% per year. As a result, large amounts of n-paraffins had to be imported and in 1980, the import was about half million tonnes. As the large percentage of the demand is represented by detergent usage, the rate of growth in the future is likely to be modest, unless a substantial breakthrough occurs in various fermentation applications².

All petroleum fractions contain varying amounts of n-paraffins; depending upon their source and boiling ranges and hence are the most promising feedstock for n-paraffin recovery. Chandra, et.al.³ have analyzed the various Indian crudes and

the corresponding 140-300°C cuts and Gujrat crudes have been found to be richest in n-paraffin content.

The fractional distillation method is unsuitable for separation of these n-paraffins, on account of overlapping of boiling ranges with other type of hydrocarbons. Urea adduct formation⁴⁻⁶ has been used to recover long straight chain paraffins, but the method has the disadvantage of higher operating cost and lower purity of n-paraffins recovered⁷.

Molecular sieve adsorption process is the most extensively used technique for separation of long straight chain paraffins from petroleum fractions containing isoparaffins, olefins, naphthenes and aromatics. The various commercial processes developed, using this technique, mainly differ in the operating conditions during the adsorption step and the type of desorbent used. The various desorbents which have been tried are low boiling n-paraffin, ammonia, nitrogen, carbon dioxide and steam.

The feasibility of using steam as a possible desorbent has not been exploited in great detail so far. If steam, which is cheaper, could be used for desorption then the subsequent separation of the product n-paraffins would be easy.

In the present work, the effect of using steam as a desorbent on the adsorption and desorption cycles has been investigated and its performance compared with that of a low

ng n-paraffin (n-pentane). The studies were conducted on
ght run kerosene obtained from Gujrat refinery, which has
highest n-paraffin content in the country. Breakthrough
as and adsorption capacities have been obtained for repeated
ption with steam without intermediate reactivation of
ular sieves. The effect of adsorption temperature has also
investigated. Height of mass transfer zone has been
ulated.

CHAPTER 2

LITERATURE REVIEW

Barrer, et.al.⁸ first discovered the ability of natural zeolites to selectively adsorb n-paraffins. They classified zeolites into three groups depending upon their ability to adsorb or exclude molecular species of a particular size- hence the name molecular sieves.

Milton, et.al.⁹ at Union Carbide in 1948, were successful in synthesising molecular sieves in the laboratory. This was a major breakthrough in zeolite research and application.

Zeolite molecular sieves are crystalline, hydrated aluminosilicates of group I and II metals viz. Na, K, Mg, Ca and Ba. Structurally, the framework of zeolites is based on an infinitely extending three dimensional network of AlO_4 and SiO_4 tetrahedra linked to each other by sharing all the oxygens. The framework consists of channels and interconnected voids, occupied by either mobile cations or water molecules.

The structural formula of a zeolite is best expressed for the crystallographic unit cell as $M_{x/n} [(AlO_2)_x (SiO_2)_y] \cdot wH_2O$ where M is the cation of valence n, w is number of water molecules and the ratio y/x has values of 1-5 depending upon the structure. The sum (x+y) is the total number of tetrahedra in the unit cell. The $[]$ portion represents the framework composition¹⁰.

Zeolite A designates the synthetic zeolite, $\text{Na}_{12} [(\text{AlO}_2)_{12} \cdot (\text{SiO}_2)_{12}] \cdot 22 \text{H}_2\text{O}$ as prepared in the Na_2O , SiO_2 , Al_2O_3 , H_2O system. The unique feature of the structure¹¹⁻¹³ is its well defined channels running parallel to the cubic axes and having a minimum free diameter of 4.2 Å. The structure consists of three different type of cavities. The largest cavity can hold a sphere with a diameter of 11.4 Å. These large cavities are linked up by eight membered rings, forming the unique main channels of the structure. The smallest isolated cavity is also nearly spherical of the order of 6.6 Å. The free diameter of these rings has been found to be 2.5 Å. The cationic exchange of Sodium with Calcium ions, enlarges the size of these windows, enabling them to readily adsorb straight chain hydrocarbons, but exclude other type of hydrocarbons. Removal of water of crystallisation leaves a stable crystalline modification, consisting of mutually connected intracrystalline voids amounting to 45 volume percent of the zeolites. The type A zeolites have an internal surface area of 700-800 sq.m./g. and an external surface of 1-3 sq.m./g. The void volume is 0.35 cm³/g.

The uniformity of pore size enables it in sieving of molecules. The mean cross sectional diameter of n-paraffin molecules is 4.9 Å, whereas iso-paraffins and cyclic molecules have minimum cross-sectional diameter 5 to 6 Å. The mean cross-sectional diameter of naphthenes and aromatics is greater than

6 A. Thus under suitable adsorptive conditions, if a mixture of hydrocarbons is passed through a bed/^{of}calcium exchanged zeolite A, the n-paraffins will be selectively adsorbed by the bed, all other hydrocarbons will pass unadsorbed.

Major commercial processes using this technique are Union Carbide's Isosiv Process¹⁴, UOP's Molex Process¹⁵, British Petroleum's Process¹⁶ and Texaco's Spectra Finishing Process¹⁷. Except for the Molex process, all others operate under vapor phase and use the fixed bed cyclic adsorption technology. The various processes differ appreciably in the operating conditions during the adsorption step and the type of desorbing fluid used to recover the product n-paraffins. Desorption fluids mentioned in the literature are low boiling n-paraffins¹⁴, ammonia¹⁵, carbon dioxide⁷, steam¹⁸, nitrogen and liquefied petroleum gas¹⁹.

The desorption step of the process is most inefficient step. Generally, the adsorption part of any process cycle occurs very rapidly. The various process cycles can be conveniently classified into four types^{1,0} as follows:

1. Thermal Swing Cycle: It operates between different temperature levels for adsorption (the lower temperature) and desorption (the higher temperature), i.e. between two isotherms. The thermal swing cycle enables high adsorbent loadings, but a cooling step is required to cool the bed. The adsorbing capacity in one cycle is the difference in loading at the two different

temperatures.

2. Pressure Swing Cycle: The process operates at essentially isothermal conditions between two pressures. The adsorption pressure is always higher than the desorption pressure. Additional adsorbate may be recovered by vacuum desorption.

As no heating and cooling is required, the cycle time is short in this case, reducing the size of adsorbent bed. Substantial amount of compression energy is required.

3. Purge Gas Stripping Cycle: A nonadsorbable purge gas is used for desorption. The purge gas reduces the partial pressure of the adsorbed species, forcing desorption. The desorbed material is carried off by the purge gas. A condensable purge gas is preferred for the sake of recycling.

4. Displacement Cycle: An adsorbable fluid or vapor displaces the material already loaded on the bed. This fluid needs separation from the adsorbate products. If the displacement fluid is more strongly adsorbed than the adsorbate on the bed, it is adsorbed displacing adsorbate on the bed. Under this condition, no stripping action due to reduction in partial pressure occurs. If a less strongly adsorbed fluid is used, the desorption occurs due to a combination of displacement and the purge stripping actions. The use of a more strongly adsorbed displacement fluid adds the additional problem of removing it in the process cycle.

Most commercial processes use low boiling n-paraffins

as the desorbent. As mentioned earlier, if steam could be used as the desorbing fluid, substantial savings in raw material and separation costs would be realized. Very little data is available on the feasibility of using steam as a desorbent. Galich, et.al.²⁰ used steam for desorption for a gasoline fraction, however the effect of steam on adsorption and desorption cycle was not investigated. Investigations at ESSO²¹, indicate: that molecular sieve life is extended by lower boiling olefins rather than steam as a desorbent. With propylene as a desorbent, no change in adsorption capacity was observed after 16 cycles, whereas with steam, the sieve capacity was reduced to two-third of the fresh sieve after 3 cycles. Saraf, et.al.¹⁸ have used steam as a desorbing fluid to recover n-paraffins from diesel oil. Steam was found to be a promising desorption fluid, however the effect of steam on continued adsorption and desorption was not studied.

There is no data on the effect of continued use of steam on the adsorption and desorption and this study was undertaken to investigate the feasibility of using steam as desorbent and its effect on the molecular sieves.

CHAPTER 3

EXPERIMENTAL INVESTIGATION

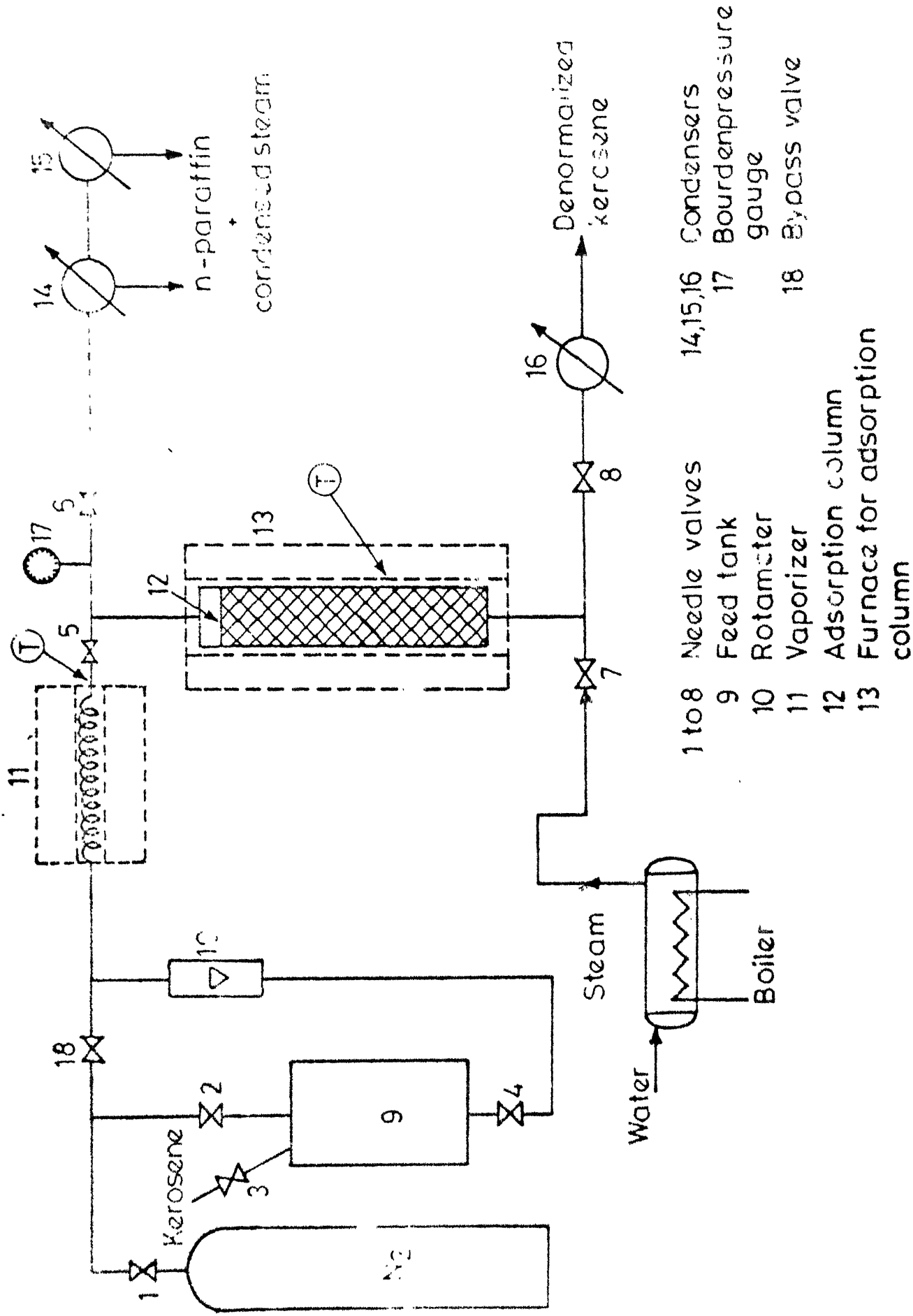
Experimental Set-Up:

The schematic diagram of the experimental set-up used is shown in figure 1.

The diameter of the fixed bed was selected from the pressure drop considerations. The adsorbent column used in the set-up was a 82 cm. long, 4.45 cm. O.D. and 3.7 cm. I.D. S.S. pipe packed with 650 grams of Linde Molecular Sieve 5A, in the form of 1/16" pellets of porosity 43% and bed diameter to pellet diameter ratio of 24. The column had appropriate inlet and outlet connections.

The column was placed in an electrically heated vertical tubular furnace, made from a 2½" I.D. and 32" long silliminite tube. Since it was difficult to maintain uniform temperature over the entire length, the furnace was divided into two independently heated sections. Both the sections were wound with 16 gauge nichrome wire of resistance 20 ohms. The chromel-alumel thermocouples were inserted from the top of the column at one third distance from each end of the column (at 11" and 24" from the top), touching the outer surface of the adsorbent column. The temperature was manually controlled within $\pm 5\%$ with the help of thermocouples in conjunction with a 0-15 mV millivoltmeter.

The feeding of kerosene was done by pressurizing it in a feedtank with nitrogen. The feedtank was a stainless steel



pipe, 12" long and $4\frac{1}{2}$ " O.D. (4" I.D.). Appropriate inlets and outlets for nitrogen gas and liquid kerosene were provided.

The kerosene was vaporized and preheated in a vaporizer. The vaporizer consisted of a coil of $\frac{1}{4}$ " copper tubing of 1.8 meters length. The column was kept inside a Lindberg furnace (type-54241) supplied with a precise automatic controller. As the automatic controller was not working properly, the temperature was controlled manually with the help of a 15 amp. variac and a 0-15 mV millivoltmeter. The feed flow rate was measured with a precision rotameter supplied by F.W. Dwyer Manufacturing Co., with the range of 10-50 cc. of water per minute. It was appropriately calibrated for kerosene feed.

Steam for desorption was generated in a boiler, which was locally constructed. The boiler was fabricated of a cast iron shell of 40 cm. O.D. Four 3 KW immersion heaters supplied by Escorts (two working and two standby) were used for the purpose of generating steam. Suitable mountings and accessories such as pressure gauge, safety valve, water level indicator, gate valves for steam outlet and water drainage were also provided.

Two vertical glass condensers in series, one $1\frac{1}{2}$ ft long and the other 1 ft long were used to condense product n-paraffins and the desorbent steam. A horizontal glass condenser was used to condense the denormalised kerosene during adsorption step. Ice water was circulated in the condensers by a $\frac{1}{2}$ hp pump.

The entire steam line and feed line after vaporizer was heated with heating tapes and wrapped with insulating rope in order to prevent condensation in the line.

Experimental Procedure:

The feed tank was charged with liquid kerosene and pressurized with nitrogen gas. The flow rate was regulated using needle valve no.4, and was measured with the rotameter. The temperature of the vaporizer column was maintained same as that of the adsorption column. The effluent stream from the adsorption column was condensed in condenser number.16 and sampled at regular intervals. Feeding was stopped after sufficient time had elapsed for the breakthrough to be achieved.

After termination of the adsorption cycle, the adsorption column was purged with nitrogen for two minute in the same direction to sweep away the unadsorbed feed in the column. Steam was used for desorption in a countercurrent direction by closing the valve numbers 5&8 and opening valve numbers 6 & 7 . The condensed stream from condenser; numbers 14&15 was withdrawn every minute. The absence of a condensed organic layer during a particular time interval marked the end of desorption. Condensed ~~steam~~ and organic layer were separated by a separating funnel. Steam rate was determined by measuring the volume of condensed steam. Mass balance on the feed was made for each run by noting the weight of the product obtained and weight of the denormalised stock.

Desorption with n-pentane was carried out cocurrently, n-pentane being charged from kerosene feedtank.

After a certain number of adsorption and desorption cycles, the adsorbent bed was reactivated by heating at 400°C for 4 hours, followed by slow cooling to the operating temperature in a stream of nitrogen.

Analysis:

For determining the n-paraffin content of the samples, the refractive index was correlated with the n-paraffin content of the samples and a linear relationship was observed. For some runs, the n-paraffin content as determined from refractive index measurements was checked with the values determined, using urea adduct method and in all cases the value was within $\pm 7\%$ and so for subsequent runs, refractive index was used to monitor the breakthrough curves and to determine the purity of the n-paraffins recovered. The calibration curve is shown in figure A-1 of the appendix. The refractive index of the effluent from condenser number 16 was monitored at regular intervals. As the refractive index is a strong function of temperature, the temperature of Abbe refractometer used, was maintained at 25°C, with the help of a thermostat.

For urea adduct analysis²² of n-paraffins, a known weight of sample was placed in a weighing bottle and stirred for one hour with an excess amount of AnalaR grade urea on a Remy

magnetic stirrer. The sample was moistened with methanol. The solid adduct was washed with benzene and filtered. The precipitate was decomposed with water. The organic layer was extracted with diethyl ether and dried with granular CaCl_2 . The straight chain hydrocarbons thus obtained were analyzed by weighing.

Materials:

All studies were made with straight run kerosene as feedstock. The kerosene was obtained from Gujrat refinery, which processes Ankleshwar crude. The boiling range of the feedstock was 140-300°C and the n-paraffin content, smoke point and density were 38.68% w/w, 24 and 0.7970 gm/cc respectively. LMS-5A, supplied by Union Carbide was used as the adsorbent. Other chemicals used, such as urea, methanol, ether solvent, anhydrous calcium chloride, n-pentane were of analytical grade.

CHAPTER 4

RESULTS AND DISCUSSION

For all the runs, the kerosene feed rate was kept fixed at 8.0 cc./min. in order to get substantial loading in a reasonable time. To study the effect of temperature, the experiments were conducted at 200° and 250°C. For a particular run, both the adsorption and desorption were carried out at the same temperature. Steam rate was kept either at 25.0 gm/min. or 15.0 gm./min. To study the effect of number of desorption cycles on adsorption, after the desorption was complete, the feeding of kerosene was again started and the procedure repeated. After a certain number of desorption cycles only, the bed was reactivated.

Mass balance on feed kerosene was made for each run.

The mass balance closure was always less than 100% presumably due to some losses in the fittings, connecting lines and the condensers. The material balance varied between 93.5-99.45% for all the runs.

The effect of number of desorption cycles without intermediate reactivation on breakthrough curve using steam as the desorbing medium at 200°C and 250°C is shown in figures 2 and 3 respectively. The exact breakthrough point could not be determined because some time was taken to fill the connecting lines and condenser from the outlet of the column to the sampling point. Although the residence time of the kerosene in the column

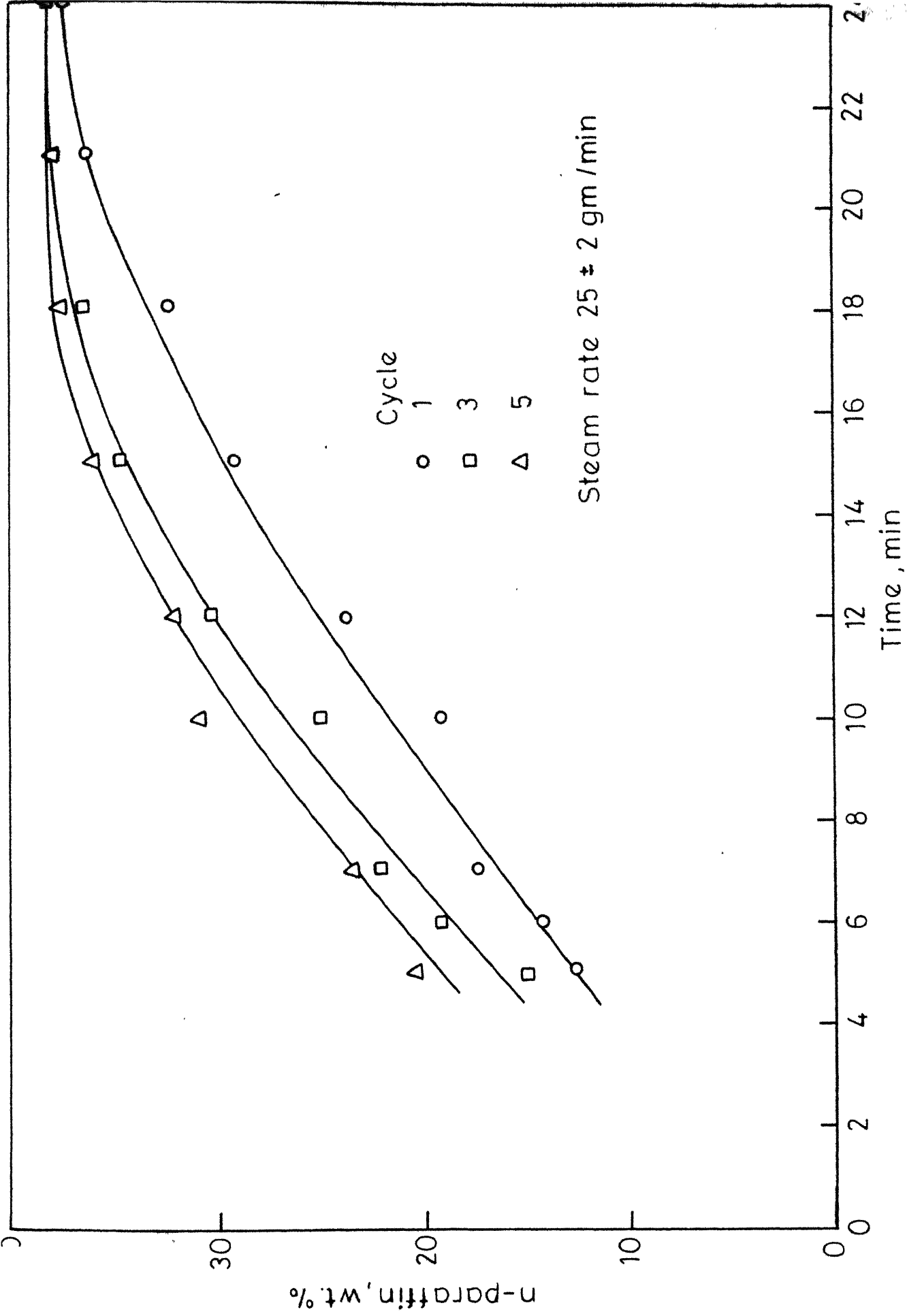


Fig. 2 - Breakthrough curves at 200°C.

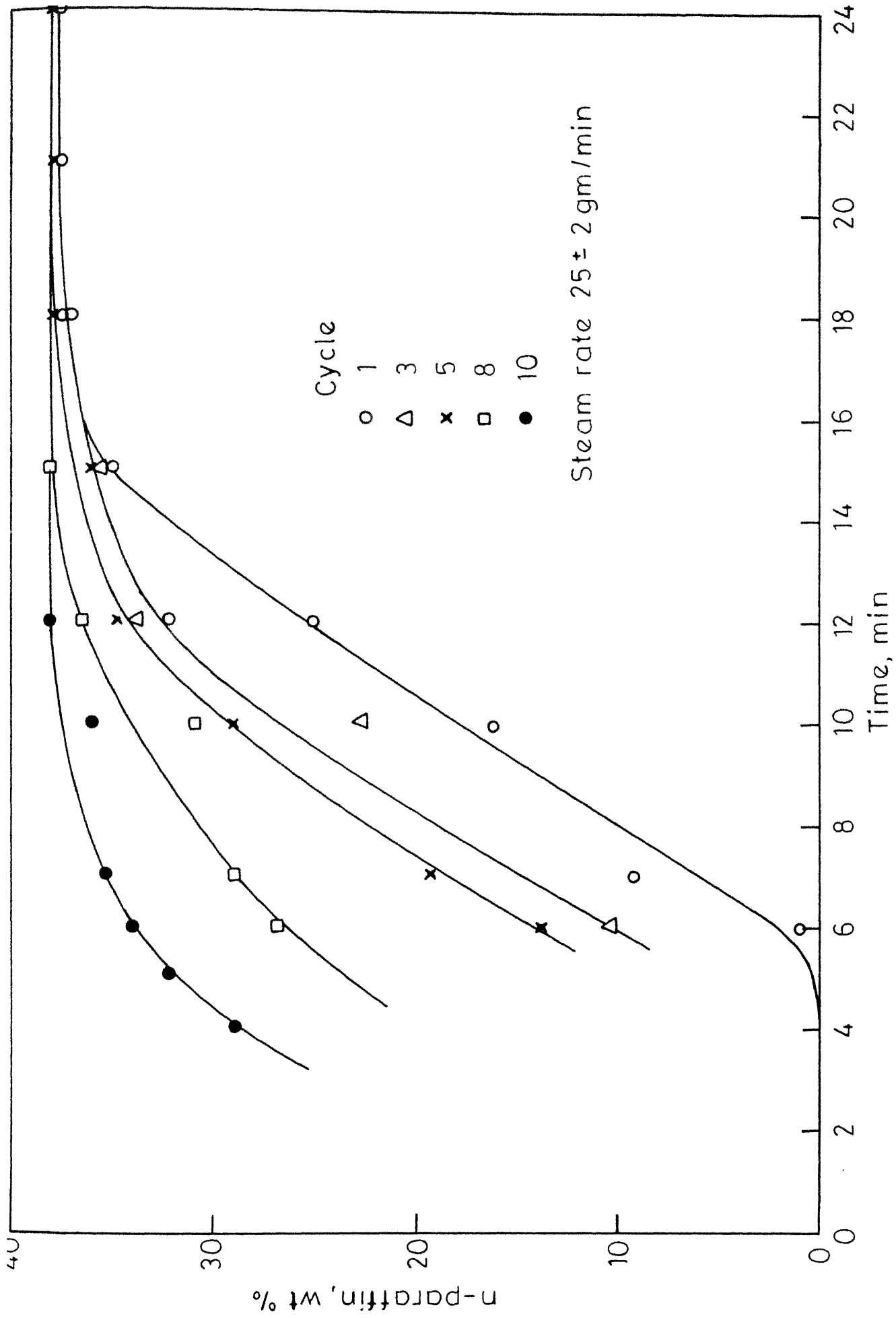


Fig. 3 - Breakthrough curves at 250°C .

was approximately 15-18 seconds, the first drop at the sampling point could be collected only after 4-6 minutes.

Comparing breakthrough curves for the first cycle at 200°C and 250°C in figures 2 and 3 respectively, it can be seen that at the higher temperature, the slope of the breakthrough curve is more and the sieves are saturated faster. This is because rate of mass transfer increases with temperature. Further, the breakthrough time reduces with increasing number of cycles, or in other words, the adsorption capacity decreases. The variation in adsorption capacity with number of desorption cycles is shown in Figure 4. For comparison, the adsorption capacity using n-pentane as desorbent is also shown.

The adsorption capacity continuously decreases with the number of cycles and at 250°C after 10 cycles, the capacity is only 22.5% of the fresh sieves. The decrease in adsorption capacity is higher at lower temperature. For example, after 5 desorption cycles at 200°C, the capacity decreased by approximately 50% compared to a decrease of 36% at 250°C for the same number of cycles. When the sieves were reactivated after 10 cycles and the adsorption repeated, the adsorption capacity was found to be almost the same as that of the fresh sieves. No change in adsorption capacity with the number of cycles was observed for n-pentane desorption. This indicates that the sieves are not permanently damaged by using steam. It seems that

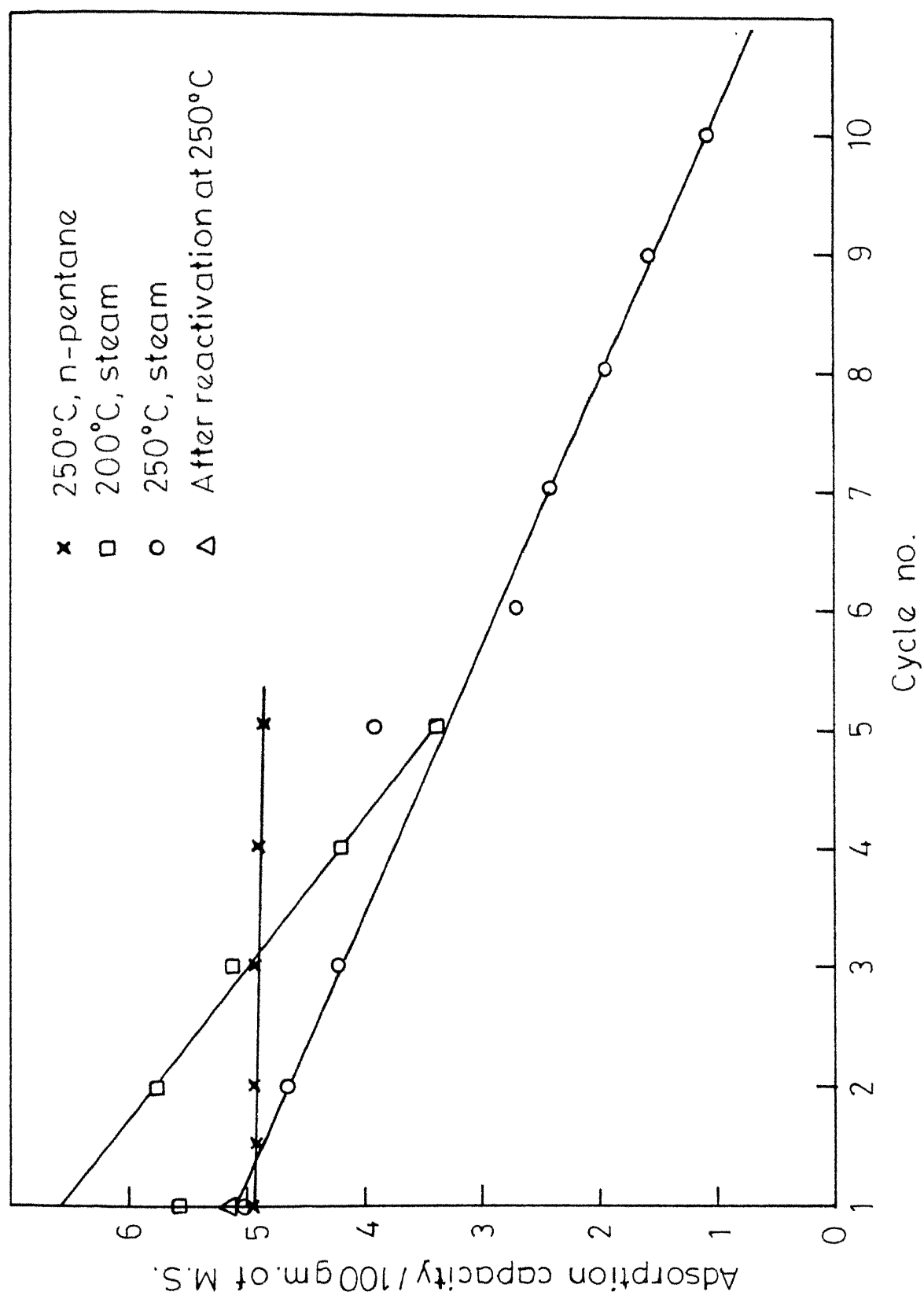


Fig 4 - Variation of adsorption capacity with cycle number.

during desorption some water is irreversibly adsorbed, thus reducing the capacity and the concentration of water in the sieves keeps on building with the number of cycles. At lower temperature, the amount of water retained in the sieves would be more and the adsorption capacity would fall at a steeper rate as experimentally observed. During reactivation (after 4 cycles at 200°C), some water was expelled from the sieves, which was approximately 3.82 gm. i.e. 0.33 mmol/gm of sieve.

It has been observed that the adsorption on molecular sieves is affected by preadsorption of polar molecules. When small amounts of water or ammonia were preadsorbed on a dehydrated zeolite, the adsorption of oxygen was drastically reduced¹⁰. This was explained by postulating that strong reaction between the mobile cation and the dipole moment of ammonia or water produces a diffusion block by clustering of water or ammonia molecules about the cation in the channels. Not much data is available on the adsorption isotherm of water on LMS-5A at 200-250°C. However, similar blocking of cation centres has been reported for NaX zeolites²³.

No appreciable change in either adsorption capacity, breakthrough time or desorption time was observed with repeated desorption without reactivation with n-pentane. The characteristics of the column when n-pentane is used as the desorbent are shown in Table 1.

TABLE 1n-PENTANE DESORPTION CHARACTERISTICS

Exhaust Time	21 minutes
Desorption Time	14 minutes
Product Recovered	22.31 gm.
Recovery	42.92%
Average Adsorption	
Capacity	4.88 gm/100 gm of M.S.

Table 1 shows the time required for desorption with n-pentane is reduced compared to steam desorption. The displacement desorption using an adsorbable medium (n-pentane), which is less strongly adsorbed than the material being desorbed involves two primary driving forces:

1. The sweeping effect of the desorbing medium flowing through sieve bed causes desorption in the same manner as when sweeping with a non-adsorbable medium.
2. The n-pentane in the desorbing medium, although less strongly adsorbed, is present in large excess during the desorption step and tend to be adsorbed, displacing the product n-paraffins from the sieve.

Due to this effecient dual action desorption mechanism, relatively rapid rates are possible. Also, since n-pentane in the desorbing medium is less strongly adsorbed than the n-paraffins in the feed stock, the desorbing medium n-pentane loaded on the sieve following the desorption step is readily displaced by the product n-paraffins during the next adsorption step, thus completing one cycle.

The breakthrough curves obtained at 250°C with n-pentane desorption are shown in figure 5. It can be seen that there is no appreciable change in the breakthrough characteristics with the number of cycles.

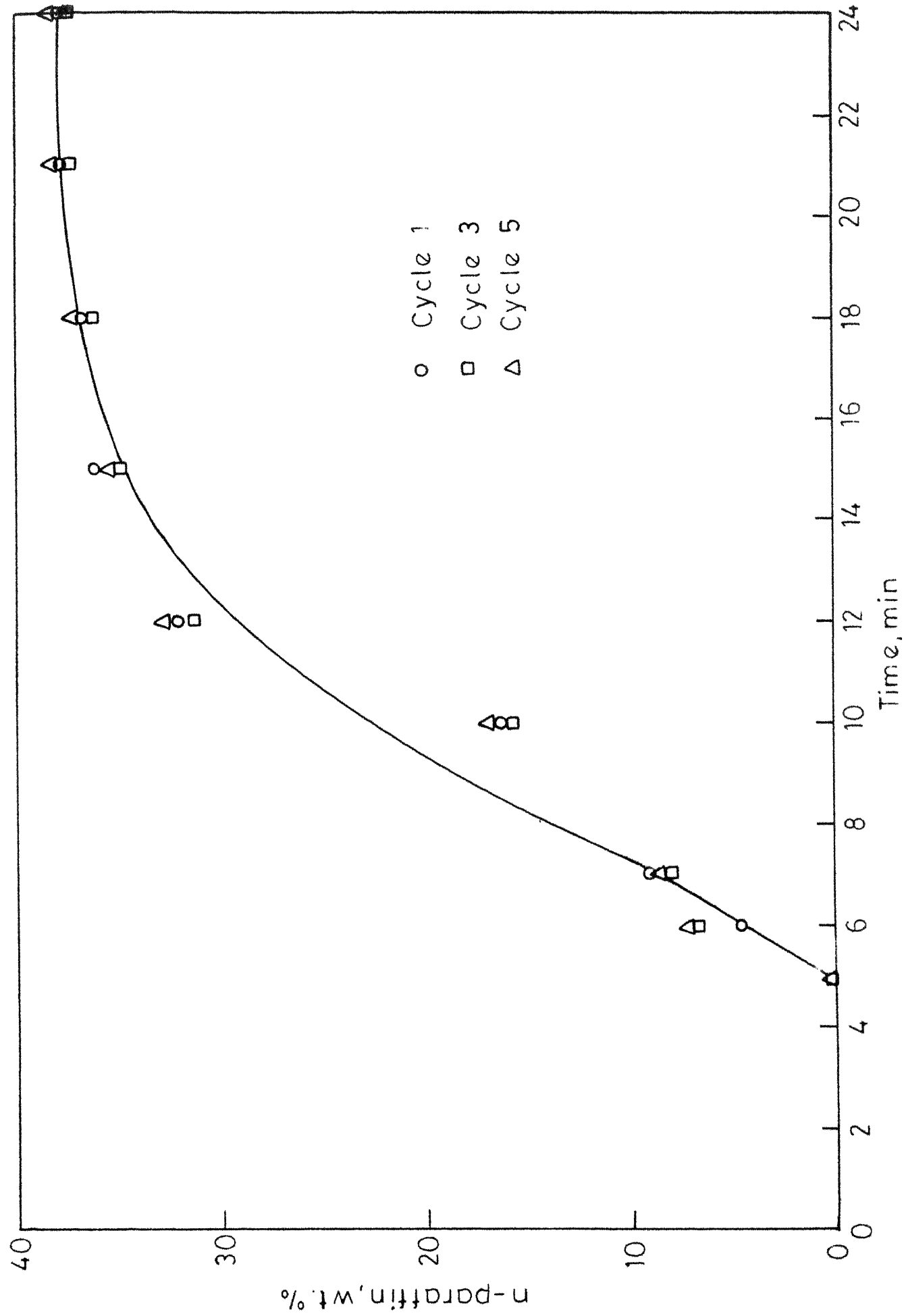


Fig. 5 - Breakthrough curves at 250°C using n-pentane as desorbent. 23

The breakthrough curves at 250°C with steam rate being kept at 15 gm/min is shown in figure 6. The curves are almost similar to those obtained with steam rate of 25 gm/min. This shows that the steam rate does not have any marked effect on the breakthrough characteristics.

For some runs, the purity of the product n-paraffins was determined using urea adduct method. It was found to be between 93-96%, which is the purity generally obtained in commercial molecular sieve column.

The recovery of n-paraffins in different cycles at different conditions is shown in table 2. The recovery is affected by the operating temperature, cycle number and the type of desorbent used. The recovery varies between 50.26% in the case of first cycle after reactivation and 17.77% after 10 cycles at 250°C. At 200°C, it is between 47.91% and 35.54%. With n-pentane as desorbent, the recovery is 42.92%.

The desorption time required in different cycles with steam at 200° C and 250°C is shown in figure 7. The desorption time continuously decreases with cycle number, because of lesser loading with increasing cycle number.

Calculation of Height of Mass Transfer Zone:

The fixed bed adsorption performance can be correlated by the mass transfer zone (MTZ) model, as proposed by Michaels²⁴.

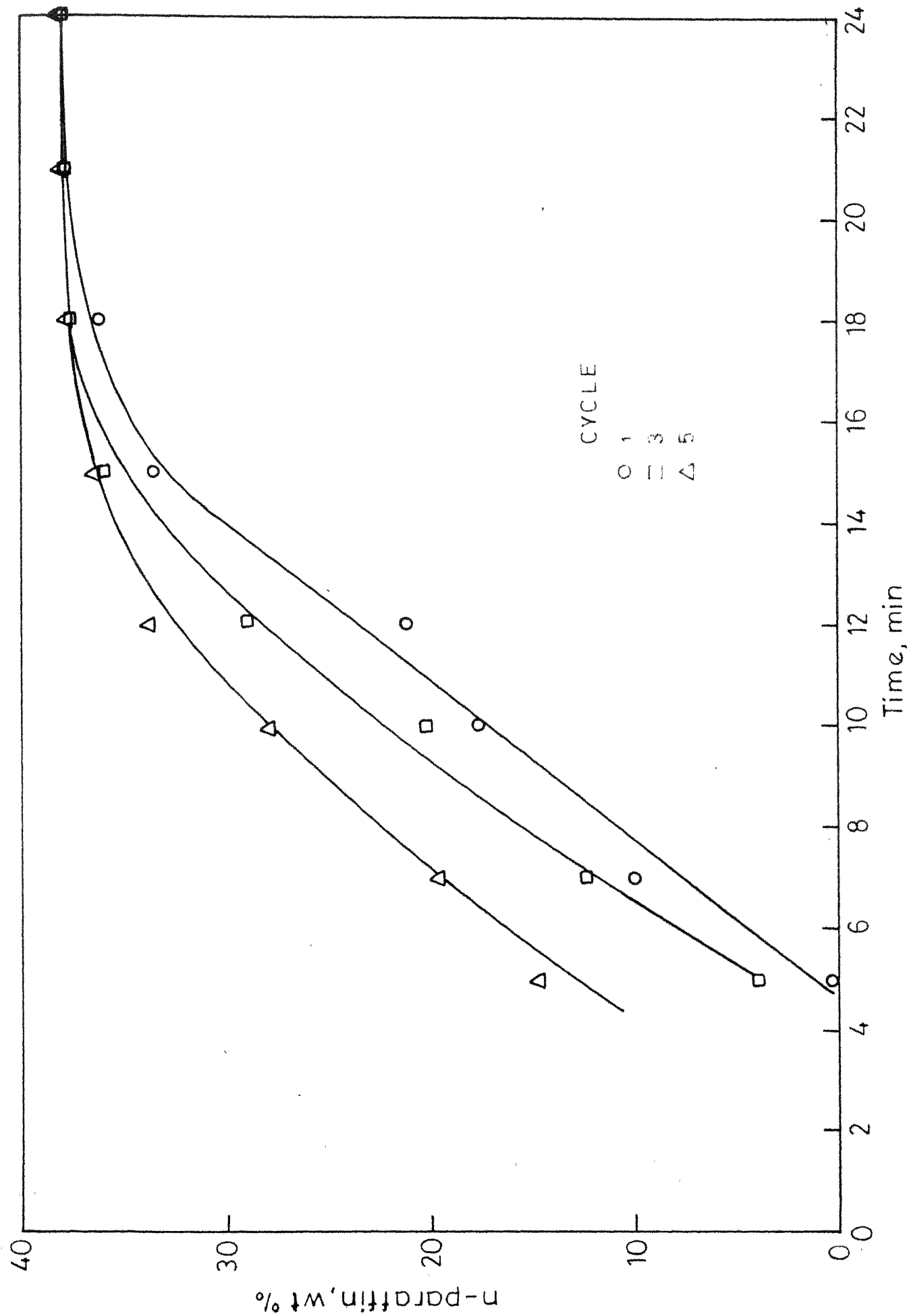


Fig. 6 - Breakthrough curves at 250°C with steam rate 15 ± 2 gm / min.

TABLE 2

RECOVERY OF n-PARAFFINS IN DIFFERENT CYCLESTemperature 250°C

Cycle number	Exhaust time minutes	n-Paraffins in feed, gm.	Product recovered, gm.	Recovery %
1	21	51.98	26.13	50.26
2	21	51.98	25.82	49.67
3	21	51.98	23.21	44.65
4	21	51.98	23.41	45.03
5	18	44.60	20.76	46.54
6	15	37.13	14.68	39.53
7	15	37.13	14.65	39.45
8	15	37.13	10.56	28.43
9	15	37.13	9.30	25.04
10	12	29.70	5.28	17.77

Temperature 200°C

Cycle number	Exhaust time minutes	n-parraffins in feed, gm.	n-paraffins recovered, gm.	Recovery %
1	24	59.41	28.47	47.91
2	24	59.41	27.63	46.50
3	21	51.98	23.54	45.28
4	21	51.98	19.30	37.12
5	18	44.60	15.84	35.54

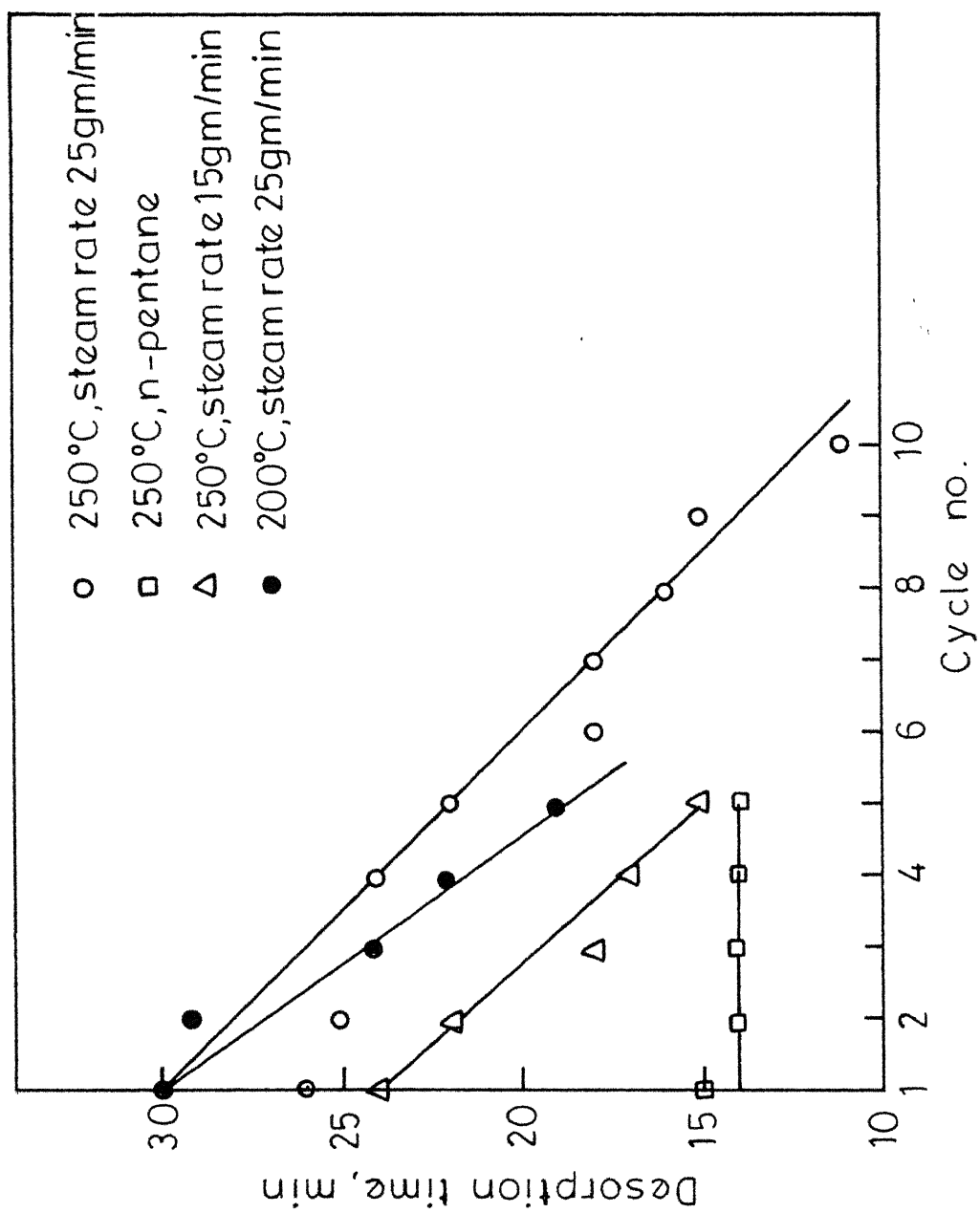


Fig. 7 - Desorption time in different cycles.

The model makes no presumption regarding the controlling adsorption rate mechanism. This model is based on the existence of an exchange zone of constant length across which the fluid concentration changes from 5 to 95%. This zone is established at the top of the column and is assumed to move down the column with a constant velocity. The zone formation time is assumed proportional to the fractional saturation of the adsorbent within the zone at the breakthrough point. The concentration profile of adsorbed species in the adsorbent bed is of a constant pattern till the adsorbate breakthrough. The zone height H_z is then expressed by the equation

$$H_z = H_T \frac{(\theta_E - \theta_B)}{(\theta_E - \theta_B) F + \theta_B} \quad (1)$$

where H_T is the total bed height. θ_E is the exhaust time, θ_B is breakthrough time and F is the fractional ability of the adsorbent within the adsorption zone to adsorb additional solute. F can be obtained by graphical integration of the experimentally obtained breakthrough curves.

To get an idea about the height of mass transfer zone, H_z was calculated using equation (1) and experimentally obtained breakthrough curves. The variation in the values of H_z with cycle number and temperature is shown in Table 3. The height of mass transfer zone should actually increase for reduced loading

TABLE 3CALCULATION OF HEIGHT OF MASS TRANSFER ZONE

Cycle number	θ_E , minutes	θ_B , minutes	F	H_z , cm. from equation(1)
<u>Temperature 250°C</u>				
1	21	4.0	0.62	95.87
3	21	3.5	0.70	91.11
5	18	2.5	0.64	102.33
3	15	2.0	0.76	89.73
10	12	1.0	0.80	91.48
<u>Temperature 200°C</u>				
1	24	2.0	0.66	108.67
3	21	1.5	0.72	102.93
5	18	1.0	0.69	110.11

on the sieves and therefore with the cycle number. However, the model cannot be rejected outright because of difficulty in exactly locating the breakthrough time. Breakthrough time, θ_B , was determined by extrapolating the experimental breakthrough curves. Equation (1) is very sensitive to the numerical value of θ_B , and hence any error in determining it may result in an incorrect conclusion. For example, if θ_B is taken as $\frac{1}{2}$ minute instead of 1 minute in 10th cycle at 250°C, (F being taken as same) the H_z comes out as 97.22 cm, which is more than the value of H_z in the first cycle. The height of mass transfer zone at 250°C and 200°C as shown in Table 3, is always more than the bed height, which is 0.82 m only. A longer column is required for correct interpretation of the results.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

The effect of steam desorption on molecular sieve adsorption of n-paraffins had been studied using the adsorptive column of LMS-5A. The feedstock was straight run kerosene (140-300°C) obtained from Gujrat Refinery. The experiments were conducted at two different temperature for a fixed feed rate. Repeated desorption with steam without intermediate reactivation was tried. The performance of steam as desorbent was compared to that of n-pentane. The significant results obtained from the experiments are:

1. Adsorption capacity decreases with cycle number. The decrease is more at lower temperature.
2. Reactivation restores the original capacity of the sieve bed to adsorb n-paraffins.
3. Adsorption capacity does not fall, with the continued use of n-pentane as desorbent.
4. Desorption time is less with n-pentane.

In the present study, the performance of n-pentane is found to be superior to that of steam. However, if the molecular sieves can be modified to reduce the equilibrium loading of water at desorption temperature, then steam can be recommended on grounds of lower cost and easier separation from product. More work is required before such a recommendation can be made.

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Recommendations:

1. Values of the height of mass transfer zone and mass transfer coefficient strongly depend on the nature of breakthrough curves. Some modifications in the experimental set-up and method of analysis is required in order to get accurate breakthrough curves. A longer column (2-3 meters) together with minimum volume in connecting lines and fittings should be used. Suitable GLC column should be developed to analyze the hydrocarbons in the kerosene range. Such an analysis will be helpful in obtaining exact breakthrough data and checking of purity of the product.
2. More data should be obtained with varying temperatures and feed rate. The effect of steam rate should be analyzed more clearly by carrying out desorption at different steam rates.
3. Pressure is an important parameter in adsorption and desorption studies. Its effect should be checked.
4. The performance of steam should be compared with other desorbents such as ammonia, carbon dioxide and LPG.
5. Some experiments should be carried out with naphtha and HSD to see the effect of feed concentration on recovery.

REFERENCES

1. LaPlante, L.J., Symoniak, M.F., Hydrocarbon Processing, 49 (12), 77 (1970).
2. Waddams, A.L., Chemicals from Petroleum, John Murray, London, 1978.
3. Chandra, D., Sodhi, J.S. and Gulati, I.B., Chemical Age of India, 22(5), 282 (1971).
4. Nelson, K.H. Grimes, M.D., Heinnich, B.J., Analytical Chemistry, 29(7), 1026 (1957).
5. Rogers, T.H., Brown, J.S. Petroleum Refiner, 36(5), 217 (1951).
6. Inge, A., Hoppe, P., Franz, H. Petroleum Refiner, 36(5), 221 (1957).
7. Mahto, J.N., Saraf, D.N., Singhal, A.K., Petroleum Hydrocarbons, 7(4), 237 (1973).
8. Barrer, R.M., Belchetz, L., Trans. Faraday Society 40, 195 (1944).
9. Milton, R.M., Molecular Sieves, Society of Chemical Industry, London, 1968.
10. Breck, D.W., Zeolite Molecular Sieves, John Wiley & Sons, New York, 1974.
11. Breck, D.W., Eversole, W.G., Milton, R.N., Reed, T.B., Thomas, T.L. J. Am. Chem. Soc. 78, 5963 (1956).
12. Barrer, R.M., Meier, W.M., Trans. Faraday Soc. 54, 1074 (1958).
13. Barrer, R.M., Meier, W.M., J. Am. Chem. Soc. 82, 1047 (1960).
14. Broughton, D.B., Lickns, A.G. Pet. Refiner, 40(5), 173, (1961).
15. Asher, W.J., Campbell, M.L., Epperly, W.R., Robertson, J.L., Hydrocarbon Processing, 48(1), 134 (1969).

16. Griesmer, G.J., Avery, W.F., Lee, M.N.Y., Hydro.Process, 446(6), 147 (1965).
17. Scott, K.A., Pet. Refiner, 43(3), 97 (1964).
18. Saraf, D.N., Darshan, P., Bhattacharya, A. Application for Indian Patent, 1977.
19. Shukla, R.P., Singhal, A.K., Saraf, D.N., Indian Chemical Engineer, 21(2), 13 (1979).
20. Galich, P.N., Tabakov, A.V., Dolinskaya, E.S., Lugovskaya, G.P., Chemical Abstract 65, 2038 (1966).
21. ESSO Research & Engg. Co., British Patent 844, 282, August 10, 1962.
22. Ijam, M.J., Ind. & Engg. Chem., Product R & D, 16, 78 (1977).
23. Advances in Chemistry Series 102, Molecular Sieve Zeolites II, American Chemical Society, Washington, 1971.
24. Michaels, A.S., Ind. Eng. Chem., 44 1922 (1952).

APPENDIX

EXPERIMENTAL RESULTS

Kerosene Feed Rate	8cc./min.
Temperature	250°C
Steam Rate	25 \pm 2 gm./min.

Cycle 1

Time, Minutes	Refractive Index
6	1.4530
7	1.4502
10	1.4478
12	1.4423
15	1.4416
18	1.4407
21	1.4406
24	1.4406

Denormalized Stock	120.11 gm.
Product Collected	26.13 gm.
Losses	6.76 gm.
Adsorption Capacity	5.06 gm./100 gm. of M.S.
Desorption Time	26 minutes

Cycle 2

Time, minutes	Ref Index	Experimentally obtained n-Paraffin, wt. %
6	1.4528	-
7	1.4493	15.72
10	1.4461	21.74
12	1.4428	29.22
15	1.4415	32.68
18	1.4411	38.10
21	1.4405	37.65
24	1.4405	37.39
Denormalized Stock		122.73 gm.
Product Collected		25.82 gm.
Losses		4.45 gm.
Adsorption Capacity		4.65 gm./100 gm. M.S.
Desorption Time		25 min.
Purity		96.07%

Cycle 3

Time, minutes	Ref. Index
6	1.4498
7	1.4478
10	1.4454
12	1.4419
15	1.4409
18	1.4407
21	1.4405
24	1.4405

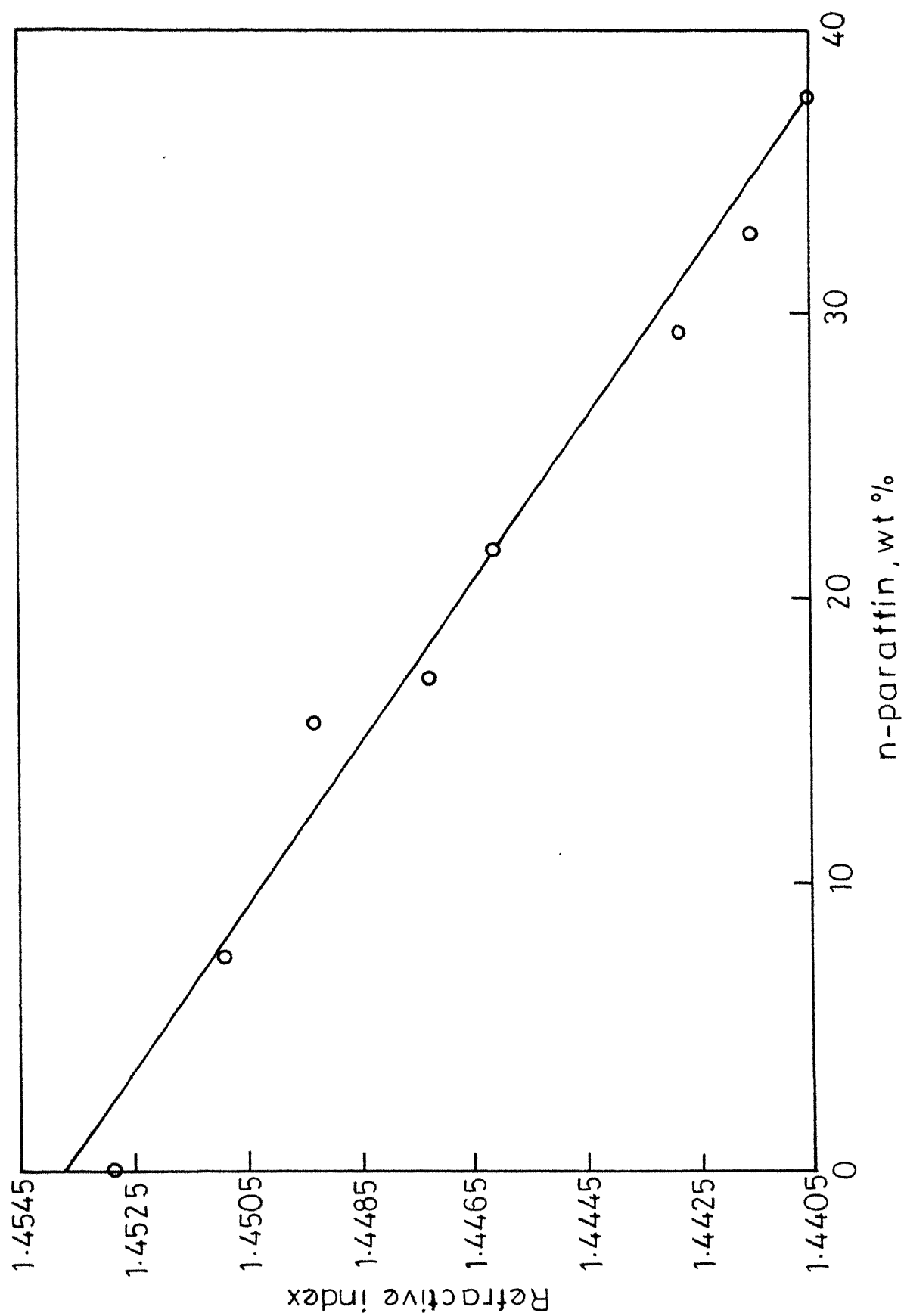
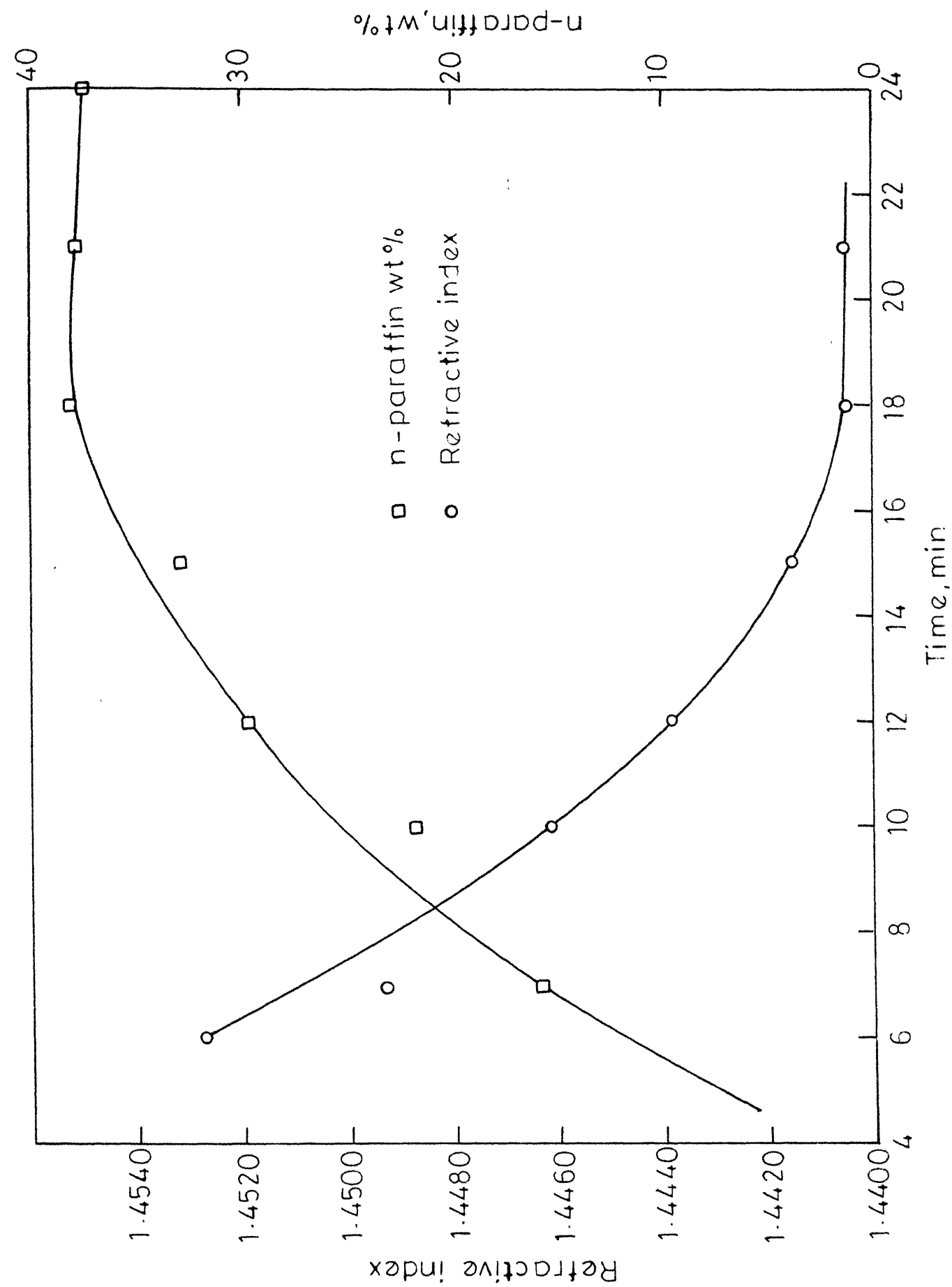


Fig. A1 - Calibration curve between refractive index at 25°C and n-paraffin wt. %.

Fig. A 2 Agreement between n-paraffin content and refractive index measurements (2nd cycle, 25.0 °C)



Denormalized Stock	125.51 gm.
Product Collected	23.21 gm.
Losses	4.28 gm.
Adsorption Capacity	4.23 gm./100 gm. M.S.
Desorption Time	24 minutes
Purity	95.4%

Cycle 4

Time, minutes	Ref. Index
6	1.4495
7	1.4485
10	1.4453
12	1.4422
15	1.4410
18	1.4408
21	1.4405
24	1.4405
Denormalized Stock	125.78 gm.
Product Collected	23.41 gm.
Losses	3.81 gm.
Adsorption Capacity	4.18 gm./100 gm. M.S.
Desorption Time	24 minutes
Purity	93.2%

Cycle 5

Time, minutes	Ref. Index
6	1.4481
7	1.4468
10	1.4435
12	1.4416
15	1.4409
18	1.4405
21	1.4405
24	1.4405
Denormalized Stock	128.30 gm.
Product Collected	20.76 gm.
Losses	3.94 gm.
Adsorption Capacity	3.8 gm./100 gm. M.S.
Desorption Time	22 minutes

Cycle 6

Time, minutes	Ref. Index
5	1.4445
6	1.4434
7	1.4426
10	1.4410
12	1.4407
15	1.4405
18	1.4405
21	1.4405
24	1.4405

Denormalized Stock	135.41 gm.
Product Collected	14.68 gm.
Losses	3.91 gm.
Adsorption Capacity	2.70 gm./100 gm. M.S.
Desorption Time	18 minutes

Cycle 7

Time, minutes	Ref. Index
5	1.4446
6	1.4433
7	1.4428
10	1.4412
12	1.4408
15	1.4405
21	1.4405
24	1.4405

Denormalized Stock	137.12 gm.
Product Collected	14.65 gm.
Losses	1.23 gm.
Adsorption Capacity	2.44 gm./100 gm. M.S.
Desorption Time	18 minutes

Cycle 8

Time, minutes	Ref. Index
6	1.4442
7	1.4435
10	1.4429

12	1.4410
15	1.4405
18	1.4405
21	1.4405
Denormalized Stock	140.20 gm.
Product Collected	10.56 gm.
Losses	2.24 gm.
Adsorption Capacity	1.97 gm./100gm.M.S.
Desorption Time	16 minutes

Cycle 9

Time, minutes	Ref. Index
5	1.4440
6	1.4431
7	1.4435
10	1.4415
12	1.4408
15	1.4405
18	1.4405
21	1.4405
Denormalized Stock	142.86 gm.
Product Collected	9.30 gm.
Losses	0.84 gm.
Adsorption Capacity	1.56 gm./100gm.M.S.
Desorption Time	15 minutes

Cycle 10

Time, minutes

Ref. Index

4	1.4437
5	1.4424
6	1.4418
7	1.4414
10	1.4410
12	1.4406
15	1.4405
18	1.4405
Denormalized Stock	145.60 gm.
Product Collected	5.28 gm.
Losses	2.12 gm.
Adsorption Capacity	1.14 gm./100gm.M.S.
Desorption Time	11 minutes

n-Paentane Desorption at 250°CCycle 1

Time, minutes

Ref. Index

6	1.4532
7	1.4506
10	1.4479
12	1.4424
15	1.4415
18	1.4408
21	1.4405
24	1.4405

Denormalized Stock	121.30 gm.
Product Collected	22.48 gm.
Losses	9.22 gm.
Adsorption Capacity	4.87 gm./100gm. M.S.
Desorption Time	less than 15 minutes

icle 2

Time, minutes	Ref.Index
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6	1.4529
7	1.4505
10	1.4480
12	1.4426
15	1.4416
18	1.4410
21	1.4405
24	1.4405

Denormalized Stock	120.80 gm.
Product Collected	22.20 gm.
Losses	10.0 gm.
Adsorption Capacity	4.95gm./100 gm. M.S.
Desorption Time	14 minutes

icle 3

Time, minutes	Ref.Index
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6	1.4530
7	1.4509
10	1.4482
12	1.4427

15	1.4416
18	1.4410
21	1.4405
24	1.4405
Denormalized Stock	121.05 gm.
Product Collected	22.42 gm.
Losses	9.53 gm.
Adsorption Capacity	4.91 gm./100 gm.M.S.
Desorption Time	14 minutes

ycle 4

Time, minutes	Ref.Index
6	1.4529
7	1.4510
10	1.4485
12	1.4428
15	1.4415
18	1.4409
21	1.4405
24	1.4405
Denormalized Stock	121.18 gm.
Product Collected	22.20 gm.
Losses	9.62 gm.
Adsorption Capacity	4.89 gm./100 gm.M.S.
Desorption Time	15 minutes

Cycle 5

Time, minutes	Ref. Index
6	1.4533
7	1.4507
8	1.4479
10	1.4422
12	1.4414
15	1.4407
18	1.4405
21	1.4405
24	1.4405
Denormalized Stock	121.70 gm.
Product Collected	22.25 gm.
Losses	9.05 gm.
Adsorption Capacity	4.78 gm./100 gm.M.S.
Desorption Time	14 minutes

Steam Rate 15 + 2 gm./min., Temperature 250°C

Cycle 1

Time, minutes	Ref. Index
5	1.4536
7	1.4502
8	1.4475
10	1.4440
12	1.4417
15	1.4409

18	1.4405
21	1.4405
24	1.4405
Denormalized Stock	120.34 gm.
Product Collected	26.15 gm.
Losses	6.51 gm.
Adsorption Capacity	5.02 gm./100gm.M.S.
Desorption Time	24 minutes

Cycle 2

Time, minutes	Ref. Index
5	1.4528
7	1.4505
8	1.4470
10	1.4434
12	1.4414
15	1.4405
18	1.4405
21	1.4405
24	1.4405
Denormalized Stock	119.78 gm.
Product Collected	25.06 gm.
Losses	8.61 gm.
Adsorption Capacity	5.11 gm./100 gm.M.S.
Desorption Time	22 minutes

Cycle 3

Time, minutes	Ref. Index
5	1.4524
7	1.4494
10	1.4465
12	1.4433
15	1.4418
18	1.4410
21	1.4405
24	1.4405
Denormalized Stock	123.81 gm.
Product Collected	22.96 gm.
Losses	6.23 gm.
Adsorption Capacity	4.49 gm./100 gm. M.S.
Desorption Time	18 minutes

Cycle 4

Time, minutes	Ref. Index
5	1.4508
7	1.4490
10	1.4462
12	1.4420
15	1.4417
18	1.4405
21	1.4405

Denormalized Stock	127.40 gm.
Product Collected	18.88 gm.
Losses	6.72 gm.
Adsorption Capacity	3.93 gm./100 gm.M.S.
Desorption Time	17 minutes

Cycle 5

Time, minutes	Ref.Index
5	1.4486
7	1.4470
10	1.4438
12	1.4420
15	1.4408
18	1.4405
21	1.4405
24	1.4405
Denormalized Stock	135.15 gm.
Product Collected	16.05 gm.
Losses	1.8 gm.
Adsorption Capacity	2.74 gm./100 gm. M.S
Desorption Time	15 minutes

Steam Desorption, Steam Rate 25 + 2 gm./min., Temperature 200°C

Cycle 1

Time, minutes	Ref.Index
5	1.4493
6	1.4489

7	1.4476
10	1.4470
12	1.4468
15	1.4434
18	1.4416
21	1.4410
24	1.4407
Denormalized Stock	116.94 gm.
Product Collected	28.47 gm.
Losses	7.59 gm.
Adsorption Capacity	5.55 gm./100gm. M.S.
Desorption Time	30 minutes

Cycle 2

Time, minutes	Ref. Index
5	1.4495
6	1.4487
7	1.4485
10	1.4470
12	1.4459
16	1.4435
18	1.4414
21	1.4409
24	1.4406
Denormalized Stock	115.72 gm.
Product Collected	27.63 gm.

Losses	9.65 gm.
Adsorption Capacity	5.73 gm./100gm. M.S.
Desorption Time	29 minutes

ycle 3

Time, minutes	Ref. Index
5	1.4484
6	1.4473
7	1.4459
10	1.4450
12	1.4436
15	1.4415
18	1.4408
21	1.4405
24	1.4405
Denormalized Stock	119.65 gm.
Product Collected	23.54 gm.
Losses	9.81 gm.
Adsorption Capacity	5.13 gm./100 gm. M.S.
Desorption Time	24 minutes

ycle 4

Time, minutes	Ref. Index
5	1.4469
7	1.4462
10	1.4448
12	1.4434

15	1.4420
18	1.4409
21	1.4405
24	1.4405
Denormalized Stock	125.63 gm.
Product Collected	19.30 gm.
Losses	8.07 gm.
Adsorption Capacity	4.21 gm./100gm.M.S.
Desorption Time	22 minutes

Cycle 5

Time, minutes	Ref. Index
5	1.4465
7	1.4455
10	1.4429
12	1.4426
15	1.4411
18	1.4407
21	1.4405
24	1.4405
Denormalized Stock	131.10 gm.
Product Collected	15.84 gm.
Losses	6.06 gm.
Adsorption Capacity	3.37 gm./100 gm.M.S.
Desorption Time	19 minutes